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ADHESION AND FRICTION OF THIN METAL FILMS

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16. Abstract Sliding friction experiments were conducted in vacuum (10^{-8} N/m ²) with thin films of titanium, chromium, iron, and platinum sputter deposited on quartz or mica substrates. A single crystal hemispherically tipped gold slider was used in contact with the films at loads of 1.0 to 30.0 and at a sliding velocity of 0.7 mm/min at 23° C. Test results indicate that the friction coefficient is dependent on the adhesion of two interfaces, that between the film and its substrate and the slider and the film. There exists a relationship between the percent d bond character of metals in bulk and in thin film form and the friction coefficient. Oxygen can increase adhesive bonding of a metal film (platinum) to a substrate.					
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ADHESION AND FRICTION OF THIN METAL FILMS

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SUMMARY

An investigation was conducted to determine the friction characteristics of various thin metallic films. The film materials included titanium, chromium, iron, and platinum. The films were deposited on quartz or mica substrates. A gold single crystal slider (111) contacted the films at loads of 1.0 to 30.0 grams and at a sliding velocity of 0.7 millimeter per minute at 23° C. Experiments were conducted in vacuum (10^{-8} N/m²) with sputter (argon) cleaned metal films and films exposed to oxygen.

The results of the study indicate that the friction coefficient for gold in contact with the metal films is dependent on adhesion at both the film-substrate and the slider-film interfaces. The d bond character of metals in both bulk and thin film form influences friction. The greater the d bond character of a metal the lower its coefficient of friction. Exposure of some metal films (platinum) to oxygen results in an increase in interfacial adhesion as well as friction.

INTRODUCTION

The advent of sputter deposition and ion plating as techniques for applying surface coatings to reduce adhesion, friction, and wear has stimulated interest in the interfacial mechanism involved when such films are used. There are two interfaces involved, and the behavior at one appears to be strongly dependent on the behavior at the other during sliding, rolling, or rubbing contact.

Both metallic and nonmetallic films have been used in tribological systems. The interest in metal films extends beyond such systems to the areas of corrosion, catalysis, and fatigue.

The objective of the present investigation was to examine the friction characteristics of sputter deposited thin metal films on the nonmetal substrates quartz and mica. A metal slider of gold with a hemispherical end slid across films approximately 2×10^{-7} meter in thickness of platinum, iron, chromium, and titanium. The films had been dc

sputter deposited on the aforementioned substrates. The gold slider was loaded against the disk surface at loads from 1 to 30 grams, and sliding was conducted at a speed of 0.7 millimeter per minute. All experiments were conducted at 23⁰ C in a vacuum of 1×10^{-8} newton per square meter. The metal films were examined as received after deposition with normal surface contaminants present and again after argon sputter cleaning of the films in vacuum.

MATERIALS

The gold, iron, platinum, and chromium were all 99.99 percent pure while the titanium was 99.97 percent pure with the principal impurity being oxygen. The gold single crystal had the (111) orientation parallel to the sliding interface. The metal films were dc sputter deposited onto quartz and freshly cleaved mica surfaces. The film thickness was measured with an optical interference microscope.

Gold was selected as a slider material because it does not form stable oxides (refs. 1 and 2) and does not strongly chemisorb active species such as water vapor (ref. 3). Furthermore, the adhesion of gold to quartz is poor in the absence of oxygen (ref. 4). Thus, special care to clean it beyond heating to 250⁰ C in a vacuum of 10^{-8} newton per square meter does not appear to be necessary. Since it is a metal it does permit an examination, however, of metal to metal interactions in adhesion and sliding friction couples.

Quartz and mica were selected as substrates for metallic film deposition for a number of reasons. First, relatively smooth surfaces can be obtained with these materials as indicated by the surface profile traces of figure 1. Thus, particularly with mica, an asperity free surface can be examined; metal films on these surfaces fairly closely match substrate topography as indicated in figure 1. Second, with thin metal films on hard substrates, such as quartz, the plastic deformation characteristics of the bulk metal become less important and the adhesion characteristics of the metal and its influence on friction more closely identified. Third, metal films and their adhesiveness to silicon dioxide and mica have been closely studied (refs. 4 to 7). These studies serve to help elucidate mechanisms for more complex sliding systems.

In references 4 to 6, as has been common practice, a harder slider is drawn across a thin film under various applied loads as a technique for measuring film adhesion to the substrate. The load at which the film is disrupted from the substrate is used as a measure of film adhesion. In this study, by using a soft extremely ductile metal like gold, particularly in single crystal form, the adhesion characteristics of the slider with the metal film can be studied.

APPARATUS

The apparatus used in this investigation was a vacuum system having built into it the capabilities for measuring adhesion, load, and friction. The apparatus also contained the surface analytical tools Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). The mechanism for measuring adhesion, loading, and friction is shown schematically in figure 2.

A gimbal mounted beam projects into the vacuum system. The beam contains two flats machined normal to each other with strain gages mounted thereon. The end of the rod contains the gold single crystal pin. As the beam is moved inward toward the disk a load is applied which is measured by a strain gage. If adhesion occurs when the load is removed, the adhesion force is measured by the bending of the beam in the direction opposite to which the load was applied (see fig. 2) after zero load is again obtained.

Tangential motion of the pin along the disk surface is accomplished through a gimbal assembly. Under an applied load the friction force is measured by a strain gage mounted normal to that used to measure load.

In the present study full-scale deflection on a conventional strip chart recorder resulted from a 10-gram adhesion or friction force giving an instrument sensitivity of ± 0.1 gram.

Multiple wear tracks could be generated on the disk specimen surface by translating the beam containing the pin. The pin slides in the vertical direction as shown in figure 2. Both AES and LEED could be used to examine any disk site desired. A gold pin was brought into contact with films of platinum, chromium, iron, and titanium deposited on quartz and mica substrates.

EXPERIMENTAL PROCEDURE

Friction experiments were performed on both clean and metal coated surfaces. After the metal coated specimens were placed in the vacuum friction and wear apparatus the system was evacuated and subsequently baked-out to achieve a pressure of 10^{-8} newton per square meter. The quartz or mica were heated in vacuum to 800°C for 1 hour to remove adsorbates. Friction experiments were then conducted on each specimen immediately upon its return to room temperature. The metal coated substrate was cleaned with argon gas bled back into the vacuum chamber to a pressure of 10 micrometers; this gas was ionized with a 1000-volt potential applied to the specimen. The argon sputter bombardment was continued for 30 minutes.

After ion bombardment the vacuum chamber was reevacuated and AES was used to determine the degree of surface cleanliness. When the surface was clean, adhesion and friction experiments were conducted. Loads of 1 to 30 grams were applied to the pin

substrate or metal coated substrate to determine the effect of load on friction. Both load and friction force were continuously monitored during a friction experiment.

RESULTS AND DISCUSSION

Clean Uncoated Quartz

Reference friction experiments were conducted with a gold (111) single crystal sliding on an uncoated quartz substrate in vacuum at various loads. Results of these reference experiments are presented in figure 3. The friction coefficient was independent of the load as indicated in the figure.

A friction coefficient of 1.0 was obtained over the entire load range. There was no evidence for gold transfer to the quartz or quartz to the gold, indicating that shear is produced at the interface rather than in either material.

Once sliding is begun, no evidence for stick-slip motion is observed with metals, as indicated in the friction trace of figure 4. The only evidence for stick-slip was observed when sliding was initiated.

The large friction coefficient observed in figure 3 indicates that the interfacial bonds formed with gold sliding on quartz are stronger than those associated with van der Waal interactions. This is in contrast to the observations of reference 8. In reference 8 with gold sliding on clean aluminum oxide in vacuum the friction coefficient obtained was one-tenth the value observed in the data of figure 3 for gold sliding on quartz. With aluminum oxide those metals which formed stable oxides interacted chemically with the oxygen of the aluminum oxide and thereby influenced friction. No evidence for gold to so interact was observed in that study. On the other hand, in this study stronger interactions with quartz appear to occur.

If gold is sputter deposited onto a quartz or fused silica substrate in pure argon, the resulting gold film is no more strongly bonded to the substrate than gold films deposited by ordinary evaporation (ref. 4). The films readily wipe off the surface. Even with ion plating as the deposition technique the results are essentially the same - namely, poor adherence. Thus, friction experiments with gold films are not practical.

Platinum Films

Platinum interacts with oxygen (ref. 9). It may therefore bond more strongly to quartz when sputter deposited. A film of platinum was sputter deposited onto a quartz surface, and the resulting films were examined in sliding friction experiments. The results obtained are presented in figure 5.

An examination of figure 5 indicates that at a 1-gram load the friction coefficient is 2.0. When the load is increased to 3.0 grams, the friction coefficient decreases to 1.0. At all loads greater than 3.0 grams the friction coefficient remained at 1.0. Microscopic examination of the wear track after sliding under a 1.0-gram load indicated a completely intact platinum film. The friction coefficient then is a measure of the platinum-gold interfacial adhesion.

When the wear track at a 3.0-gram load is examined, platinum is found to have broken away from the substrate as indicated in figure 6. In this figure the black region is the exposed quartz and the lighter material to either side is the platinum film.

The friction coefficient obtained at loads in excess of 1.0 gram is essentially the same as that observed with gold in contact with the quartz substrate in figure 3. The initial temptation is, upon examining figure 6, to indicate that the film has broken up and the friction is essentially that of the gold-quartz interface. An examination of the friction trace of figure 7(a) shows it to be markedly different from that of figure 4 for the gold pin sliding on quartz. The entire trace has a very marked stick-slip character, typical of metal to metal adhesion and friction.

The force to initiate shear of the platinum-quartz interface and to initiate shear within the film about the contact area is high as indicated by the large initial breakaway force of figure 7(a). As tangential motion commences, the friction force decreases to a steady-state stick-slip condition. Shear within the film now simply involves metal ahead of the slider and to either side. It is the shearing at the interface and in the film which accounts for the stick-slip character of the friction trace.

If the platinum film is exposed to oxygen at atmospheric pressure for 30 minutes and if the vacuum system is then re-evacuated, the friction trace of figure 7(b) is obtained. The friction coefficient rises to a high value and remains there. It did not decrease after sliding began as it did in figure 7(a). An examination of the platinum film after sliding indicated the film was nearly intact. Thus, it appears that the presence of oxygen increases the adhesion of the platinum film to the quartz. This results in gold sliding on oxygen covered platinum rather than shear occurring between the platinum-quartz interface.

The increase in adhesion following the adsorption of oxygen has been observed by others. In reference 4 the adhesion of sputter deposited gold to a fused silica surface was found to increase when oxygen was bled into the vacuum system with the argon gas used for dc sputtering.

A similar event may be occurring in reference to the data of figure 7(b). With the admission of oxygen, the adhesion of platinum to the quartz may increase. The adherence of sputtered films to adsorbates has been demonstrated with other film substrate combinations (ref. 10).

In considering the friction characteristics of thin films deposited on substrates two interfaces must be examined as indicated in figure 8. There is an interface between the

slider and the film (interface A) and a second interface between the film and the substrate (interface B). When a load is applied to the soft gold slider, it will deform plastically and adhesion to the metal film will occur. With tangential motion shear will occur in the weakest region. It could be at interface A, interface B, in the film between interfaces, in the slider bulk, or in the bulk substrate.

The data obtained with the platinum films indicate that the region where shear occurs with sliding is at interface B (see fig. 6). When oxygen is admitted, the interface is strengthened and shear takes place principally at the gold-platinum interface (interface A).

Titanium Films

There have been many studies which have concluded that the adhesion of metal films to oxide substrates is directly related to the free energy of oxide formation of the deposited material. That being the case, very strong adhesion should occur for titanium to the quartz substrate. A titanium film was sputter deposited on a quartz substrate. Friction experiments were conducted on the film both in the clean state (as determined by AES analysis) and after being at atmospheric pressure for 30 minutes, as was done with platinum. The friction results obtained are presented in figure 9.

The data of figure 9 indicate that at a 1.0-gram load the friction coefficient is 7.0. It decreases with increasing load to a value of 1.5. This decrease in friction may be associated with interfacial recrystallization of the gold single crystal slider as was observed in another investigation under similar conditions of load and speed (ref. 11).

After sliding, an examination of the titanium wear track indicated that it had not been dislodged from the quartz substrate at all during sliding. Gold was found to have transferred to the titanium. Thus, the shear occurring in the gold indicated that the adhesive bond at both the titanium-quartz and titanium-gold interfaces were stronger than the cohesive binding strength in the gold (3.68×10^5 J/g-at.).

The oxide film on the titanium surface reduced the friction coefficient between the gold and titanium (fig. 9). This is consistent with normal metal to metal interaction - namely, that oxides, in general, reduce friction.

Chromium Films

Chromium forms a stable oxide, but it is not quite as stable as titanium (ref. 12). The chromium was deposited on a quartz substrate in the same manner as the platinum and titanium. The results of friction experiments with these films are presented in figure 10.

Examination of figure 10 indicates that the friction coefficient decreased with increased loading as was observed with titanium. As with titanium, the film remained intact after sliding. The friction trace exhibited the characteristic stick-slip behavior of metal to metal contact as indicated by the friction trace of figure 11.

The sliding friction experiments with bulk metals in contact with bulk metals conducted herein seem to indicate a fundamental relation between d valence bond character of metals and friction. The greater the percent of d valence bond character the lower the friction coefficient as indicated by the data of figure 12. The percent of d valence bond character data were obtained from reference 13.

Friction data obtained with titanium, chromium, iron, and platinum films on quartz at a 1.0-gram load were compared to the d valence bond character. The results obtained are presented in figure 13.

The data of figure 13 indicate a decrease in friction coefficient with an increase in the percent of d valence bonding. Even at heavier loads both the iron and platinum were disrupted (iron only partially) from the quartz surface while the titanium and chromium were not.

Iron Films on Mica

Recent studies with mica substrates indicate very strong adhesion of metal to this surface. Friction experiments were therefore conducted with iron films sputter deposited on both quartz and mica substrates. The results obtained are presented in figure 14.

At the light loads friction is considerably higher with mica than observed for the quartz substrates (fig. 14). At the heavier loads there was partial disruption of the iron film on both substrates. This disruption is indicated in the photomicrograph of figure 15.

With mica it has been suggested that potassium ions as well as oxygen may participate in the adhesive bonding of a metal to a mica substrate (ref. 7). This, then, may account for the higher friction observed with mica in figure 14.

In reference 7 the metal bonding to mica was gold. Gold is the slider used in this investigation. Once the iron film is disrupted and direct contact is made with the substrate, these forces may account for the differences in friction seen in figure 14.

CONCLUSIONS

The following remarks are based on the results of this investigation with gold sliding on various metal films deposited on quartz and mica substrates:

1. The greater the percent d bond character of a metal the lower the friction in both

bulk metal and thin film.

2. Friction is dependent on the adhesive bonding of the metal film to the substrate as well as to the film.

3. Oxygen can increase the friction for metal couples when one member of the couple is a film, and oxygen increases the adhesion of the metal film to the substrate as was observed with platinum on quartz.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, February 19, 1976,
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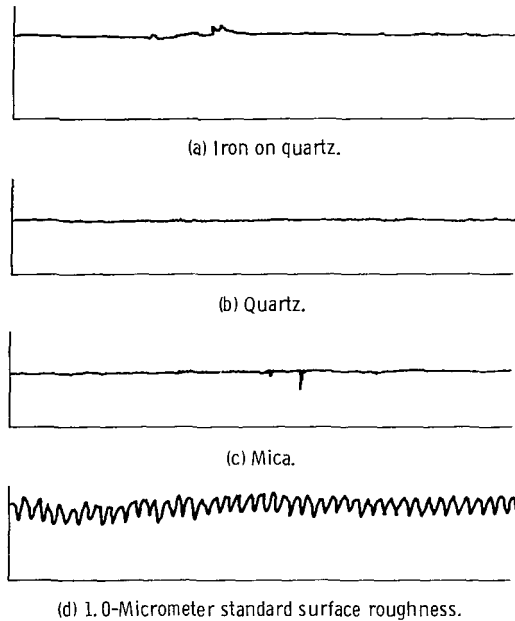
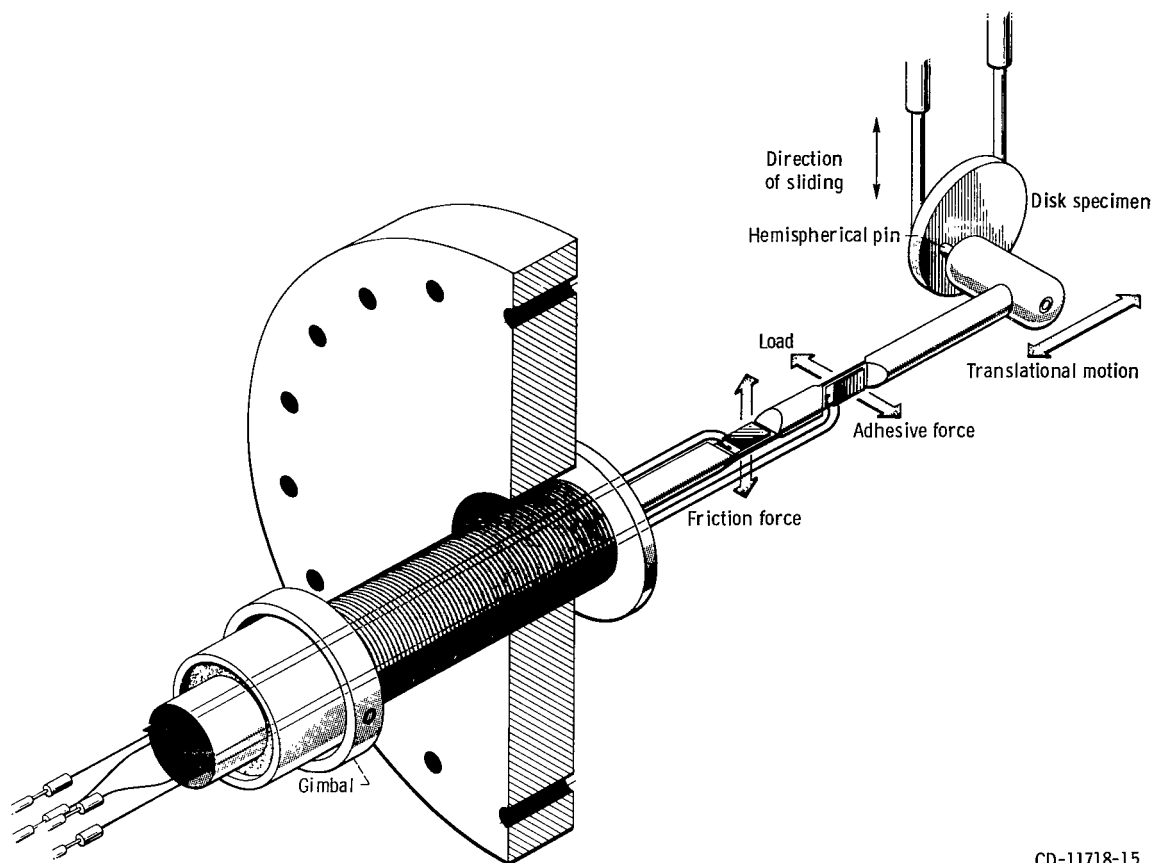


Figure 1. - Surface profiles of various materials used in sliding friction studies.



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Figure 2. - High-vacuum friction and wear apparatus.



Figure 3. - Friction coefficient for gold (111) single crystal sliding on quartz flat. Sliding velocity, 0.7 millimeter per minute; temperature, 23⁰ C; pressure, 10⁻⁸ newton per square meter.

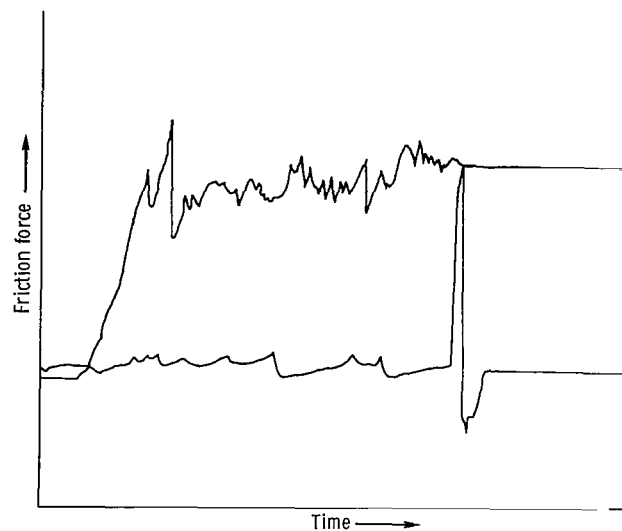


Figure 4. - Friction trace for gold (111) crystal sliding on quartz surface. Sliding velocity, 0.7 millimeter per minute; temperature, 23° C; pressure, 10^{-8} newton per square meter; load, 30 grams.

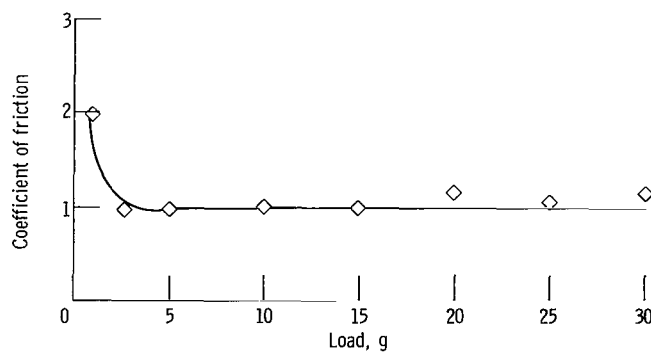


Figure 5. - Coefficient of friction as function of load for 2×10^{-7} meter platinum film sputter deposited on quartz substrate. Sliding velocity, 0.7 millimeter per minute; temperature, 23° C; pressure, 10^{-8} newton per square meter.

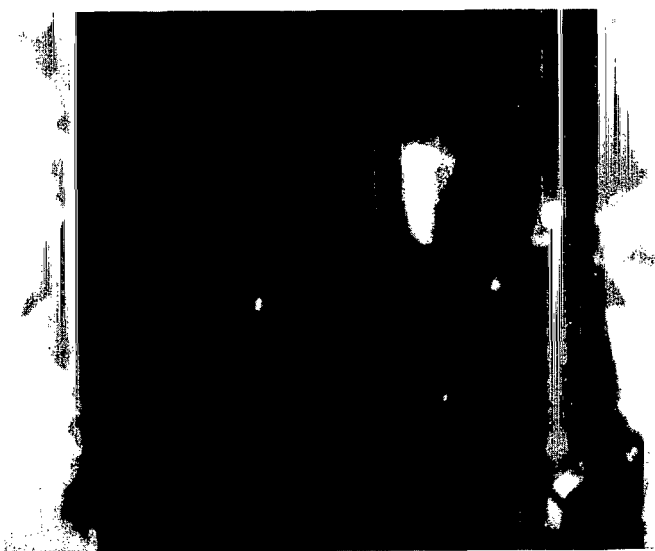


Figure 6. - Wear track of platinum film on quartz substrate indicating film disruption with sliding. Sliding velocity, 0.7 millimeter per minute; temperature, 23° C; pressure 10^{-8} newton per square meter; load, 30 grams.

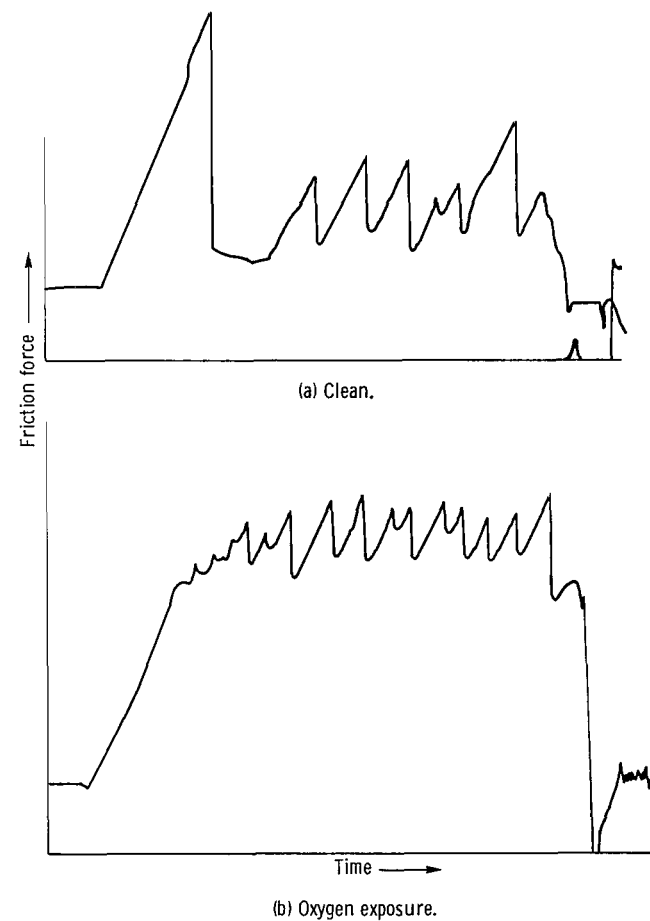


Figure 7. - Friction traces for gold pin sliding on platinum film sputter deposited on quartz substrate. Sliding velocity, 0.7 millimeter per minute; temperature, 23° C; pressure, 10^{-8} newton per square meter; load, 30 grams.

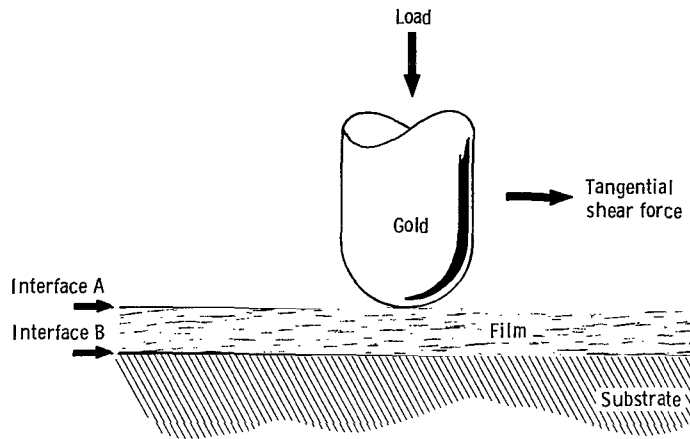


Figure 8. - Sliding friction interfaces with thin films.

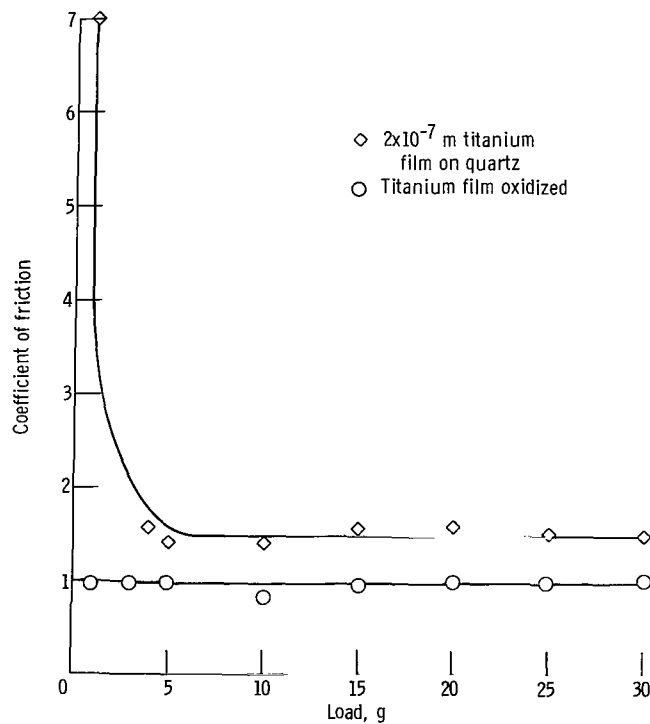


Figure 9. - Coefficient of friction as function of load for 2×10^{-7} meter titanium film sputter deposited on quartz substrate and that same film oxidized. Sliding velocity, 0.7 millimeter per minute; temperature, 23°C ; pressure, 10^{-8} newton per square meter.

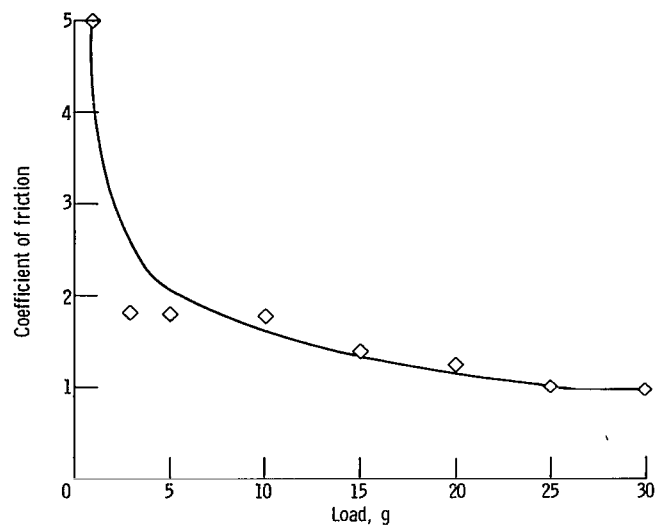


Figure 10. - Coefficient of friction as function of load for quartz and 2×10^{-7} meter chromium film on quartz. Sliding velocity, 0.7 millimeter per minute; temperature, 23°C ; pressure, 10^{-8} newton per square meter.

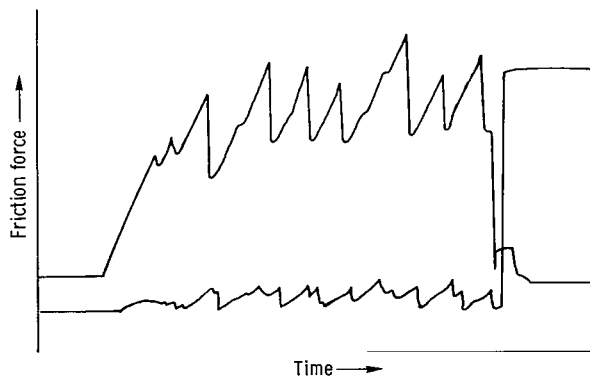


Figure 11. - Friction trace for gold (111) crystal sliding on 2×10^{-7} meter chromium film sputter deposited on quartz substrate. Sliding velocity, 0.7 millimeter per minute; temperature, 23°C ; pressure, 10^{-8} newton per square meter; load, 30 grams.

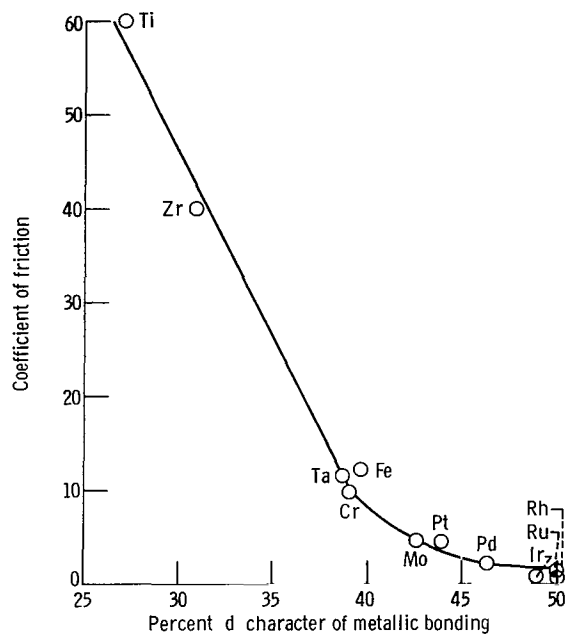


Figure 12. - Coefficient of friction as function of percent d bond character for various metals. Sliding velocity, 0.7 millimeter per minute; temperature, 23° C; pressure, 10^{-8} newton per square meter; load, 1 gram.

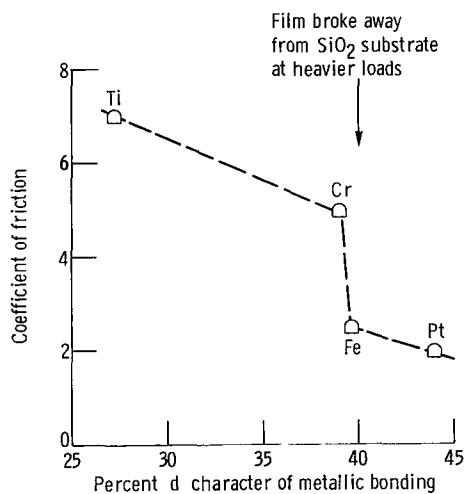


Figure 13. - Coefficient of friction of various metal films sputter deposited on quartz substrate as function of d bond character. Sliding velocity, 0.7 millimeter per minute; temperature, 23° C; pressure, 10^{-8} newton per square meter; load, 1 gram.

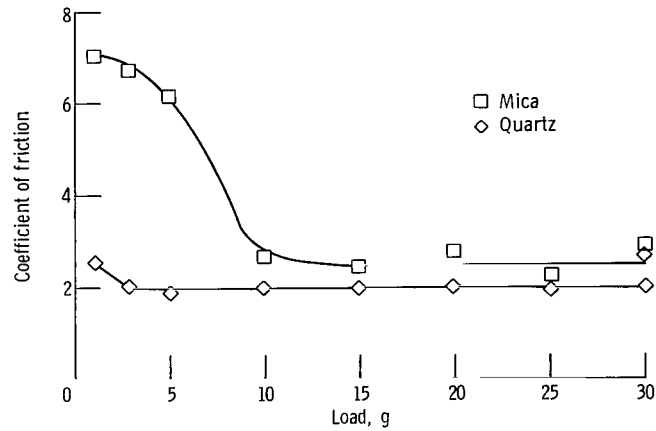


Figure 14. - Friction coefficient for iron film sputter deposited on mica and quartz substrates. Sliding velocity, 0.7 millimeter per minute; temperature, 23° C; pressure, 10^{-8} newton per square meter.



Figure 15. - Wear track of iron 2×10^{-7} meter film sputter. Deposited on mica substrate after single pass of gold slider. Sliding velocity, 0.7 millimeter per minute; temperature, 23° C; pressure, 10^{-8} newton per square meter; load, 30 grams.



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